

## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to a polybutylene terephthalate system resin oriented film, the multilayered stretched film which has it, and saccate wrapping. . This invention fabricates in more detail the polybutylene terephthalate system resin obtained by continuous polymerization method. There are few foreign matters (fish eye), and it excels in molding stability, especially extension stability, and also is related with the polybutylene terephthalate system resin oriented film excellent in appearance, internal visibility, design nature, etc., the multilayered stretched film which has it, and saccate wrapping.

[0002]

[Description of the Prior Art] When polybutylene terephthalate system resin excels [ crystallization rate ] in molding workability greatly as compared with polyethylene terephthalate system resin, Since it excels in a mechanical property, an electrical property, etc., in the injection-molding-work field, it is widely used as engineering plastics from before. Furthermore, the characteristics which polybutylene terephthalate system resin has, such as a smell retaining property and chemical resistance, are accepted, and it is observed also in the film shaping and packaging material field in recent years. By the way, the manufacturing method of polybutylene terephthalate system resin, The ester interchange method for passing through an ester exchange reaction with the diol component which uses as the main ingredients the dicarboxylic acid ester component which uses the ester derivative of terephthalic acid, such as dimethyl terephthalate, as the main ingredients, and 1,4-butanediol, There is the direct polymerization method for passing through a direct esterification reaction with the diol component which uses as the main ingredients the dicarboxylic acid component which uses terephthalic acid as the main ingredients, and 1,4-butanediol, There are a batch polymerization process of furthermore performing the polycondensation reaction which carries out polymers quantification with a batch method after an early esterification reaction (oligomerization), and a continuation polymerization process which performs from an esterification reaction to a polycondensation reaction continuously. From the manufacturing-cost side, the continuation polymerization process using terephthalic acid and 1,4-butanediol is overwhelmingly made advantageous. However, when polymerizing according to a continuation polymerization process, in order to operate a polymerization plant continuously for a long time (from several months to one years or more), The prolonged holdup in a system carries out super-increased viscosity, and as a result, it may become non-melt at the time of shaping, and may become a foreign matter, or it deteriorates during a reaction, and in a polymer component, it may become extremely large, it may deposit [ an esterification reaction catalyst may become

insoluble, ], and a viscosity difference with the main product may generate an aggregate, and may serve as a foreign matter. These super-hyperviscous things and sludges turn into a fine foreign matter which actualizes when a thin film is used especially, and is called a fish eye, Even if an extension fracture is caused, and the productivity of a film can be reduced extremely or it can fabricate it as a film, by the foreign matter effect by a fish eye The fall of a mechanical strength, The situations which are not preferred, such as causing an appearance defect, the visibility fall of contents, and the fall of the design nature by the ink jump at the time of printing, were invited, and it had become a big problem in the film field which thinks especially transparency and printing nature as important.

[0003]

[Problem(s) to be Solved by the Invention]. Fabricate the polybutylene terephthalate system resin which this invention is a basis of such a situation and was obtained by continuous polymerization method. There are few foreign matters (fish eye), and it excels in molding stability, especially extension stability, and also is made for the purpose of providing the polybutylene terephthalate system resin oriented film excellent in appearance, internal visibility, design nature, etc., the multilayered stretched film which has it, and saccate wrapping.

[0004]

[Means for Solving the Problem]In order that this invention person may attain said purpose, as a result of repeating research wholeheartedly, as a raw material, When a film of predetermined thickness is used, and the number of a fish eye more than a certain size uses polybutylene terephthalate system resin with few foreign matters below with a specific value, it finds out that that purpose can be attained and came to complete this invention based on this knowledge. Namely, this invention is obtained by (1) continuous polymerization method, And a polybutylene terephthalate system resin oriented film, wherein the number of a fish eye with a size [ in a film with a thickness of 50 micrometers of resin ] of not less than 20 micrometers is obtained using polybutylene terephthalate system resin which is below 20 piece / 100 cm<sup>2</sup>, (2) A multilayered stretched film which laminates an oriented film given in the 1st paragraph with other resin layers, (3) A multilayered stretched film given in the 2nd paragraph which laminates a resin layer which has adhesion performance on one side of a polybutylene terephthalate system resin oriented film at least, (4) The 2nd paragraph that provides at least one layer of layers which oxygen permeability under 0% of relative humidity environment becomes from resin lower than polybutylene terephthalate system resin, or a multilayered stretched film given in the 3rd paragraph, And either the (5) 1st paragraph thru/or, and the 4th paragraph are provided with saccate wrapping which heat seals a pars basilaris ossis occipitalis of a film of a statement, and/or two sides or more.

[0005]

[Embodiment of the Invention]The polybutylene terephthalate system resin from which the polybutylene terephthalate system resin oriented film of this invention was obtained by continuous polymerization method as a raw material is used. As this polybutylene terephthalate system resin, The dicarboxylic acid component which uses terephthalic acid and/or its ester derivative, for example, methyl ester, ethyl ester, propyl ester, etc. as the main ingredients, After mainly carrying out the esterification reaction of the diol component which uses 1,4-butanediol as the main ingredients continuously under existence of an esterification reaction catalyst and carrying out a polycondensation reaction continuously subsequently, the polybutylene terephthalate system resin obtained by extracting from a polymer draw die is mentioned. Here, as for the terephthalic acid and/or the terephthal acid ester derivative as a dicarboxylic acid component, it is preferred to occupy more than 50 mol % of a total dicarboxylic acid component, and to occupy more than 80 mol %, and it is still more preferred to occupy more than 95 mol %. As for 1,4-butanediol as a diol component, it is preferred to occupy more than 50 mol % of all the diol components, and to occupy more than 80 mol %, and it is still more preferred to occupy more than 95 mol %. In this invention, as an example of dicarboxylic acid components other than terephthalic acid, Phthalic acid, isophthalic acid, 4,4'-diphenyldicarboxylic acid, 4,4'-diphenyl ether dicarboxylic acid, 4,4'-diphenyl ketone dicarboxylic acid, 4, and 4'-difenoxycarboxylic acid, Aromatic dicarboxylic acid, such as 4,4'-diphenylsulfone dicarboxylic acid, 2, and 6-naphthalene dicarboxylic acid, 1, 2-cyclohexanedicarboxylic acid, 1, 3-cyclohexanedicarboxylic acid, Alicyclic dicarboxylic acid, such as 1,4-cyclohexanedicarboxylic acid, malonic acid, Ester species with these methyl, ethyl, propyl alcohol, etc., such as aliphatic dicarboxylic acid, such as succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, and sebacic acid, is mentioned. One sort may be used for these and may be used for them combining two or more sorts.

[0006]On the other hand, as an example of diol components other than 1,4-butanediol, Ethylene glycol, a diethylene glycol, a polyethylene glycol, Propylene glycol, 1,3-propanediol, polytetramethylene ether glycol, 1,5-pentanediol, neopentyl glycol, 1,6-hexanediol, Aliphatic series diol, such as 1,8-octanediol, 1,2-cyclohexanediol, 1,4-cyclohexanediol, 1,1-cyclohexane dimethylol, Aromaticdiol, such as alicyclic diol, such as 1,4-cyclohexane dimethylol, xylylene glycol, 4,4'-dihydroxybiphenyl, 2,2-bis(4'-hydroxyphenyl)propane, and a bis(4-hydroxyphenyl) sulfone, etc. are mentioned. These may use one sort and may use it combining two or more sorts. For example, glycolic acid, m-hydroxybenzoic acid, para-hydroxybenzoic acid, Hydroxycarboxylic acid and alkoxy carboxylic acid, such as 6-hydroxy-2-naphthalene carboxylic acid and p-beta-hydroxyethoxybenzoic acid, And stearyl alcohol, benzyl alcohol, stearic acid, benzoic acid, Monofunctional ingredients, such as t-butyl benzoic acid and benzoylbenzoic acid, tricarballic acid, Trimellitic acid, trimesic acid, pyromellitic acid, gallic acid, trimethylolethane, One sort chosen from the polyfunctional ingredients,

trimethylolpropane, glycerol, pentaerythritol, etc., of three or more organic functions, such ester species, etc. or two sorts or more can be used as a copolymer component. As polybutylene terephthalate system resin in this invention, The diol component which uses as the main ingredients the dicarboxylic acid component which uses terephthalic acid as the main ingredients, and 1,4-butanediol, It is preferred that it is resin produced by polymerizing continuously, and it is preferred that it is especially resin produced by using terephthalic acid and 1,4-butanediol as the main raw material, and polymerizing continuously.

[0007] Since what has the intrinsic viscosity  $[\eta]$  measured in the mixed solvent with a temperature of 30 °C of phenol/tetrachloroethane (weight ratios 1/1) in the range of 0.6 - 3.0 dl/g as polybutylene terephthalate system resin in this invention is suitable for shaping of the film, it is preferred. A film moldability falls [ this  $[\eta]$  ] by less than 0.6 dl/g, and thickness nonuniformity does not occur, or, in the case of inflation molding, a bubble is not stabilized, and it is not desirable. On the other hand, if 3.0 dl/g is exceeded, extrusion torque becomes high, load is applied to apparatus, or resin leakage occurs from the joined part of apparatus, and it is not desirable. More desirable intrinsic viscosity is 0.8 - 2.0 dl/g, and is the range of 0.9 - 1.3 dl/g still more preferably. As polybutylene terephthalate system resin in this invention, It is preferred that the number of a fish eye with a size [ in a film with a thickness of 50 micrometers of resin ] of not less than 20 micrometers is resin which is below 20 piece / 100 cm<sup>2</sup>, and it is resin which is below ten piece / 100 cm<sup>2</sup>. If many fish eyes exist, even if an extension fracture occurs frequently, and the continuously stable productivity of a film falls greatly or the appearance of a film is not only bad, but serves as a film fortunately in the stretching process in a film manufacturing process, When unevenness was not completed in a film surface when the film was wound up, or contents do not look beautiful when it is processed into a bag etc. and fills up with contents, or it prints on a film, an ink jump occurs, it becomes a printing trouble and a problem occurs. The fish eye level of the number below 20 piece / 100 cm<sup>2</sup> is a level which is not conspicuous even if the above-mentioned trouble does not occur or it generates, and is substantially satisfactory. If it is large-sized molding equipment when it generates once, material loss will serve as several 10 kg - 100 kg of numbers, especially an extension fracture becomes a double trouble where a product is not obtained on the other hand in the meantime, and its problem is dramatically large from a point of productivity. If the number of fish eyes exceeds 20 piece / 100 cm<sup>2</sup>, an extension fracture will come to occur extremely. It is considered for a slight extension fracture in a foreign matter portion to come to spread that the number of fish eyes of an extension fracture increases bordering on 20 piece / 100 cm<sup>2</sup>.

[0008] Fundamentally, the manufacturing method of the polybutylene terephthalate system resin used by this invention is based on the continuous manufacturing method of common use of polybutylene terephthalate system resin. Namely, in the singular number or two or more

esterification reaction tubs said dicarboxylic acid component which uses terephthalic acid and/or its ester derivative as the main ingredients, and said diol component which uses 1,4-butanediol as the main ingredients, It is the method of carrying out the bottom esterification reaction of churning, transporting oligomer as an acquired esterification reaction output to a polycondensation reactor, being decompression and an elevated temperature in the singular number or two or more polycondensation reactors, and performing a polycondensation reaction continuously under existence of a polycondensation reaction catalyst under elevated-temperature ordinary pressure. As a manufacturing method of polybutylene terephthalate system resin in this invention, The method of carrying out direct polymerization of the dicarboxylic acid component which uses terephthalic acid as the main ingredients, and the 1,4-butanediol continuously using the diol component used as the main ingredients is preferred, and the method of carrying out direct polymerization continuously, using terephthalic acid and 1,4-butanediol as a main raw material is more preferred. The resin obtained by the polycondensation reaction is usually continuously transported to a polymer draw die from the pars basilaris ossis occipitalis of a polycondensation reactor, and being extracted and water-cooled by strand shape, after water cooling, it is cut by the cutter and let it be granules, such as a pellet type and chip shape. As an esterification reaction catalyst in said manufacturing method here, For example, titanium alcoholates, such as tetramethyl titanate, tetraisopropyl titanate, and tetrabutyl titanate, They are mentioned by titanium phenolates, such as tetraphenyl titanate, etc. as a typical thing, and the amount used, For example, in the case of tetrabutyl titanate, 30-300 ppm is usually preferably selected in 50-200 ppm as a titanium atom to the theoretical yield of polybutylene terephthalate system resin. [0009]A tin compound, a magnesium compound, a lime compound, etc. other than said titanium compound can be used as an esterification reaction catalyst, for example. As a polycondensation reaction catalyst, said esterification reaction catalyst added at the time of an esterification reaction can be succeedingly used as a polycondensation reaction catalyst, In this case, although it is not necessary to add a new catalyst, said same catalyst as the esterification reaction catalyst added at the time of an esterification reaction may be added further. In said esterification reaction and/or a polycondensation reaction, besides said catalyst, Phosphorus compounds, such as orthophosphoric acid, phosphorous acid, hypophosphorous acid, polyphosphoric acid, and those ester, metal salt, Reaction auxiliary agents, such as alkaline metals, such as sodium hydroxide, sodium benzoate, magnesium acetate, and calcium acetate, or an alkaline earth metal compound, Phenolic compounds, such as 2,6-di-t-butyl-4-octylphenol and pentaerythryl tetrakis [3-(3',5'-di-t-butyl-4'-hydroxyphenyl) propionate], Thioether compounds, such as the dilauryl 3, 3'-thiodipropionate, and pentaerythryl tetrakis (3-lauryl thiodipropionate), Triphenyl phosphite, tris (nonylphenyl) phosphite, Anti-oxidants, such as phosphorus compounds, such as tris (2,4-di-t-buthylphenyl) phosphite, Other additive agents, such as release agents, such

as long chain fatty acid represented by paraffin wax, microcrystallin wax, polyethylene wax, montanic acid, and montanic acid ester and its ester, and silicone oil, may be made to exist. In the case of a multi stage continuation polymerization plant, the 2nd step polycondensation tub uses the horizontal-type reaction vessel provided with the agitating device which has a horizontal rotation axis in many cases. Within this reaction vessel, a polycondensation reaction is 235-280 \*\* usually preferably advanced further under churning under decompression of 667 Pa or less the temperature of 235-265 \*\*, and of 1333 Pa or less usually. And in order to remove a foreign matter and to carry out reduction of the fish eye in the continuous manufacturing method of the above-mentioned polybutylene terephthalate system resin in this invention. It is desirable to install a filter in the main product stream way of a before [ from the exit of the first esterification reaction tub / the exit of a polymer draw die ], and to pass this filter for the main output.

[0010]Although any, such as metal Wynd, a laminated metal mesh, a metallic nonwoven fabric, and a porous metal plate, may be sufficient here as a filter medium which constitutes a filter, the laminated metal mesh from a viewpoint or the metallic nonwoven fabric of filtration accuracy is preferred. As shape of a filter, a basket type, a disk type, Although it may be which form, such as a leaf disk type, a tube type, a flat type cylinder type, and a pleated type cylinder type, when melt viscosity filters low oligomer, A viewpoint to a tube type or flat type cylinder types, such as detergency, are preferred, and when filtering the high prepolymer and polymer of melt viscosity, the leaf disk type from viewpoints of resistance to pressure, the treatment flow rate per unit area, etc. or a pleated type cylinder type is preferred. It is preferred to make filtration accuracy into the range of 0.5-50 micrometers from fields, such as filtration efficiency, absolutely of a filter, When melt viscosity filters low oligomer, the range of 0.5-30 micrometers is more preferred, and when filtering the high prepolymer and polymer of melt viscosity, it is more preferred to consider it as the range of 5-50 micrometers. Here, as shape of a filter, they may be which form, such as a flat type, a cylinder type, and a candle type. As for filtration accuracy, it is preferred absolutely to consider it as the range of 0.5-50 micrometers from fields, such as filtration efficiency. Drawing 1 is a flow chart which shows one example of the continuous manufacturing method of polybutylene terephthalate system resin in such this invention, The dicarboxylic acid component which uses as the main ingredients the terephthalic acid prepared by the raw material preparation tubs 1, and/or its ester species, the raw material mixture containing the diol component etc. which use 1,4-butanediol as the main ingredients -- the 1st-step esterification tub 2 -- subsequently to the 2nd-step esterification tub 3 it supplies, an esterification reaction is carried out, and oligomer is made to generate subsequently, this oligomer -- the 1st step polycondensation tub (for example, vertical mold reactor) 4 -- it transporting subsequently to the 2nd step polycondensation tub (for example, horizontal-type reactor) 5, and, After advancing a polycondensation reaction furthermore and

making polymer generate, it transports to the polymer draw die 6, polymer is extracted, and it is considered as granules, such as a pellet type and chip shape, by the pelletizer 7. Said filter may be installed in which place from the exit of the 1st-step esterification tub 2 to the exit of the polymer draw die 6, and may be installed in one place or two or more places. A setting position effective in especially tailing is installing in the place from the exit of the 2nd-step esterification tub 3 to the exit of the polymer draw die 6, and is installing in the place from the exit of the 2nd step polycondensation tub 5 to the exit of the polymer draw die 6 still more preferably. It is not that to which a polymerization apparatus and polymerization conditions are limited above in this invention, It is important to obtain the polybutylene terephthalate system resin which gives the oriented film which removed the foreign matter in the middle of the channel of the main output of the polybutylene terephthalate system resin manufactured continuously in short by installing a filter, and in which reduction of the number of fish eyes was carried out to it.

[0011]Although resin of various intrinsic viscosity is mainly obtained by operating condition change of the 2nd step polycondensation tub, polybutylene terephthalate system resin by said continuous polycondensation process, When you would like to obtain hyperviscous resin furthermore, or when reduction of the tetrahydrofuran which are the main side reaction output needs to be carried out, The resin-grains-like object acquired with continuous polymerization method under an inert gas atmosphere and/or decompression of about 13-1333 Pa, Usually, it is a temperature lower 5-50 °C than the melting point of resin, and a desirable temperature lower 10-40 °C than the melting point, and it is also possible to usually heat-treat and carry out a solid phase polycondensation reaction in about 5 to 20 hours, performing a flow etc. so that granules may not adhere. In the polycondensation reaction of polybutylene terephthalate system resin in this invention, When many foreign matters are contained in the polymer obtained when solid state polymerization was used together and a filter was not installed in manufacture of the resin which is to solid state polymerization and it fabricates to film state, it may become a cause of the product tampering trouble called a fish eye. The oriented film of this invention can be obtained by film-izing the polybutylene terephthalate system resin produced by doing in this way, and carrying out stretching treatment further by a publicly known method. As the method of film-izing, the resin fused, for example is extruded to plate-like, The T die casting method which takes over continuously with a roll and makes a plate-like film, It swells in the shape of a balloon, extruding melting resin continuously from an annular die, and adjusting internal pneumatic pressure, Although the air-cooling tubular film process cooled with cold blast, the water-cooled tubular film process on which water is poured and which is cooled while extruding continuously [ it is same and ] from an annular die and controlling an outer diameter by regulation rings, such as metal, the calendar method using a roll, etc. are mentioned, T pressure die casting and the tubular film process with which melt extruding is possible without touching with the open air are preferred. In shaping of a multilayer

film, a multilayer film can be obtained using a publicly known multilayering device (a multimer knee hold T die, a stack plate dice, a feed block, a multilayer inflation dice) etc.

[0012]When fabricating a film, it is preferred to adjust a cylinder temperature and die temperature so that resin temperature may be about 230-290 \*\*. Although the thickness of the film obtained varies with the purpose to be used, when it is a monolayer film, it is after extension, is usually 10-100 micrometers, and, in the case of a multilayer film, is usually 15-200 micrometers. The thickness of the film for presenting extension changes with draw magnification in 1 axis extension or biaxial extension again. If the thickness of the film after extension is too thin, the extension fracture by a stretching process becomes being easy to generate, or improvement in the thickness accuracy of an extension front film becomes difficult, the thickness nonuniformity of a product becomes large, and it is not desirable. On the other hand, if the thickness of the film after extension is too thick, many problems will come to arise -- it must extend by excessive power by a stretching process, and device load cannot become large or it cannot extend depending on an extension method. 12-80 micrometers, still more preferably, the range of desirable thickness is 15-50 micrometers with the monolayer film after extension, and the range of it is 30-80 micrometers still more preferably 20-120 micrometers in a multilayered stretched film. Even if the oxygen barrier property of polybutylene terephthalate system resin is quite high and it remains as it is, can prevent the oxidation degradation of contents highly, but. As objects for a package, such as half a lifetime products, such as pastes as which advanced oxygen barrier property is required, and raw edible perishables, Resin whose oxygen permeability under 0% of relative humidity environment is lower than polybutylene terephthalate system resin, For example, the condensate of aliphatic series nylon films, such as 6 nylon and 66 nylon, aliphatic dicarboxylic acid, and aromatic diamine, Or it is also possible to process the common-name K-coat etc. which carried out the coat of multilayer structure with half-aromatic nylon and the partial saponification thing (common name EVOH) of an ethylene-vinylacetate copolymer which make representation the condensate of aromatic dicarboxylic acid and aliphatic diamine, or the emulsion of vinylidene chloride resin.

[0013]What is necessary is just to design oxygen barrier property resin and its thickness there be no regulation in particular about the thickness at the time of multilayering with resin whose oxygen barrier property is higher than these polybutylene terephthalate system resin, and become oxygen barrier property required for preservation of contents after extension. For example, as lamination for the package of roast ham, that whose overall thickness is 40-80 micrometers in polybutylene terephthalate system resin (12.5%) / adhering resin (6.3%) / 6 nylon (31.2%) / adhering resin (6.3%) / linear shape low-density-polyethylene (43.7%) grade is good. % in ( ) shows the ratio of thickness. As an example of other multilayer structure. \*\* PBT / adhering resin PBT / adhering resin / polyethylene-system-resin PBT / adhering resin /



polypropylene resin PBT / adhering resin / polyamide resin / adhering resin / polyethylene system resin, or polypropylene resin PBT / adhering resin / EVOH resin / adhering resin / polyethylene system resin. Or a polypropylene resin polyethylene system, or a polypropylene resin / adhering resin / PBT / adhering resin is mentioned. The above PBT shows polybutylene terephthalate system resin, in addition the example of each resin is as follows.

Polyethylene system resin : Ultra low density polyethylene, low density polyethylene, Straight-chain-shape low density polyethylene, high density polyethylene, an ethylene-vinylacetate copolymer, Polypropylene resins, such as an ethylene-ethyl acrylate copolymer : The gay PP, Adhering resin, such as the C4 copolymerization PP, the C6 copolymerization PP, the C8 copolymerization PP, and a terpolymer : Maleic anhydride modified polyethylene system resin, Polyamide resin, such as glycidyl-methacrylate polyethylene-copolymer system resin and glycidyl-methacrylate acrylic-acid-polyethylene-copolymer system resin: The various above-mentioned nylon etc. [0014]As for stretching treatment, it is preferred to carry out below with the melting point from near the glass transition temperature of polybutylene terephthalate system resin, and 5 times as many ranges of draw magnification are preferred from length and each 1.5 times as many transverse direction. Since an extension fracture will not occur or orientation crystallization will not take place if extension temperature is too low, the mechanical properties of a film do not become high and are not preferred. If extension temperature is too high, a film does not milk, or intensity is not revealed and it is not desirable. If draw magnification is too low, stretching unevenness will occur, the film of uniform thickness will not be obtained, or if too high, an extension fracture will be carried out and a film will not be obtained. It is important to make extension temperature and an extension rate into the respectively suitable range. For example, in PBT monolayer 1 axis extension, in one [ 3 to 6 times the draw magnification / the extension temperature of 50-75 \*\*, and / of this ], monolayer, or multilayer simultaneous biaxial extension, the extension temperature of 50-70 \*\* and 2.5x2.5 times - about 3.5x3.5 times draw magnification are desirable. Usually, in order for an oriented film to make the dimensional stability after stretching treatment reveal, beyond extension temperature performs a heat setting below with the melting point, but. Although conditions change considerably with resin which in extension of PBT resin heat setting temperature is about 200 \*\* in the case of a monolayer film, and has been multilayered in the case of the multilayer film, it is advantageous to carry out in 80-200 \*\*.

[0015]When fabricating a film, a publicly known additive agent, for example, a phenol system, The silica for demonstrating antioxidants, such as the Lynn system, sulfur systems, and an amine system, and anti BUROKKIGU performance, Bridge construction organicity particles, such as inorganic particles and bridge construction PMMA, such as zeolite, talc, a glass bead, and silicone particles, and bridge construction polystyrene, The ester species of the calcium salt of fatty acid including calcium stearate, sodium salt and a polyethylene system wax, and

polyhydric alcohol, etc. may add various colorant, a release agent, etc. further as lubricant. When these additive agents carry out film shaping, they may be blended in a raw material, and the masterbatch beforehand adjusted to high concentration may be used for them, diluting it suitably at the time of shaping. Next, the saccate wrapping of this invention is obtained by heat sealing the pars basilaris ossis occipitalis of the monolayer oriented film or multilayered stretched film produced by doing in this way, and/or two sides or more. When using this monolayer oriented film and a multilayered stretched film as a bag for a package, heat is usually applied to film comrades who piled up, such as heat sealing or impulse heat sealing, and, specifically, it is processed into a bag by the method of once fusing and connecting. When a film is fabricated to tube shape, it is possible to create a bag-like object by carrying out the seal only of the one direction used as a pars basilaris ossis occipitalis, but. When the film on a flat surface is produced by a T-die method etc., in order to use a bag, bag manufacture processing can be carried out by both method seal methods of three which heat seal the pillow package which heat seals a pars basilaris ossis occipitalis and is processed into saccate after carrying out the seal of the both-ends comrade of a film so that it may become tube shape, and both ends and a pars basilaris ossis occipitalis. It is also possible to produce a polygonal bag, in order to serve as the forcing bag at the time of filling up a paste state thing and whipped cream with manufacturing bags to a long triangle or to give design nature, and to attach the port for collecting waste fluid. Although polybutylene terephthalate system resin can also heat seal the present state, In order to heat seal at low temperature more and to make bag manufacture processing efficiency high, there is the method of using adhesives for an above-mentioned multilayer film (what laminated resin whose melting point is lower than outermost layer resin for the innermost layer) and monolayer film, and carrying out dry laminate of the resin, such as polyethylene with the low melting point. When these low melting point resins are used for an innermost layer, the cobwebbing of the resin which melted in order not to fuse does not happen, but a result of a heat seal part becomes beautiful, and polybutylene terephthalate system resin of the outermost layer is desirable.

[0016]

[Example]Next, although an example explains this invention still in detail, this invention is not limited at all by these examples.

Except having considered it as the channel which mentioned the installation channel of example 1 filter later, The raw material preparation tubs 1 are supplied at a rate of 1.8 mol of 1,4-butanediol to 1 mol of terephthalic acid using the same manufacturing installation as what was shown in drawing 1, It transported to the 1st-step esterification tub 2 adjusted to the temperature of 230 \*\*, and pressure 0.1013MPa, and to raw material 100 weight section, tetrabutyl titanate 3.14 weight section was supplied, the esterification reaction was carried out under churning in holding time 2 hours, and oligomer of 87.3% of the rate of an esterification

reaction was obtained. Then, the oligomer is transported to the 2nd-step esterification tub 3 adjusted to the temperature of 240 \*\*, and pressure 0.1013MPa, The esterification reaction was further advanced under churning for 1 hour, oligomer of 98.0% of the rate of an esterification reaction was obtained, the polycondensation reaction was transported and carried out to the 1st step polycondensation tub 4 which adjusted the oligomer to the temperature of 250 \*\*, and pressure 6.65kPa for 2 hours, and the prepolymer of intrinsic viscosity 0.24 dl/g was obtained. Then, after passing the pleated type cylinder type filter which makes a filter medium the laminated metal mesh which has the filtration accuracy of 20 micrometers absolutely in the middle of piping which transports the prepolymer to the 2nd step polycondensation tub 5, It transports to the 2nd step polycondensation tub 5 adjusted to the temperature of 260 \*\*, and the pressure of 66.5 Pa, Advance a polycondensation reaction further by holding time under churning for 4 hours, obtain polymer of intrinsic viscosity 1.20 dl/g, transport the polymer to the polymer draw die 6 with a gear pump, and it extracts to strand shape, The polybutyrene-terephthalate-resin pellet (PBT-1) was manufactured by cutting by the pelletizer 7 and considering it as a pellet type. Here, the rate of an esterification reaction and intrinsic viscosity were measured by the method shown below, respectively.

[0017]Rate of esterification reaction profitable \*\*\*\* oligomer was dissolved in N,N-dimethylformamide, electric conductivity titration was carried out in the ethanol nature solution of the 0.1 mol % potassium hydrate, acid value was measured, and it computed with the following formula from the acid value value  $[X \text{ (meq/g)}]$ .

The rate of an esterification reaction = the viscosity of the solution in which the mixed solvent of phenol/tetrachloroethane (weight ratios 1/1) was made to dissolve  $[(9.083-X)/9.083] \times 100$  intrinsic-viscosity profitable \*\*\*\* polymer by the concentration of 1.0 g/dl, It asked by measuring at 30 \*\* using an Ubbelohde viscometer. It has a T die for the obtained polybutyrene-terephthalate-resin pellet, After supplying the cylinder temperature to the 1 axis extrusion machine set as 270 \*\* and carrying out melting extrusion to film state, what was fabricated on the 50-micrometer-thick film was obtained by quenching with the metal cooling rollers held in temperature of 58-62 \*\*. When the number of the fish eye was measured by the method shown below, they were 6.3 piece / 100 cm<sup>2</sup>.

About the film which was obtained as for the number of fish eyes, five places of an area of 10 cm (100 cm<sup>2</sup>) around were observed with the stereoscopic microscope 50 times the magnification of this, the number of the fish eye which has a core with a size [ in each part ] of not less than 20 micrometers was counted, and the average value was computed. Next, it has a T die using this polyester system resin (PBT-1), after supplying the cylinder temperature to the 1 axis extrusion machine set as 270 \*\* and carrying out melting extrusion to film state, \*\*\*\*\* was obtained on the 150-micrometer-thick film by quenching with the metal cooling rollers held in temperature of 25-27 \*\*.

[0018]The oriented film with a thickness of about 38 micrometers which carried out stretching treatment of this film to the lengthwise direction by one 4 times the draw magnification [ the extension temperature of 50 ° and ] of this with the drawing machine of the T.M. long company was obtained. The extension success percentage was shown in the 1st table. The pleated type cylinder type filter which makes a filter medium the metallic nonwoven fabric which has the example 2 absolute filtration accuracy of 30 micrometers was used, The filter was installed in the middle of piping between the 2nd step polycondensation tub 5 and the polymer draw die 6, And the polybutyrene-terephthalate-resin pellet was manufactured like Example 1 except having made the operating condition of the 2nd step polycondensation tub 5 into 255 °, 70 Pa, and holding time 2.5 hours. The rate of an esterification reaction of oligomer in 1st-step esterification tub 2 exit in that case 87.0%, The rate of an esterification reaction of oligomer in 2nd-step esterification tub 3 exit 98.1%, The intrinsic viscosity of the prepolymer in 1st step polycondensation tub 4 exit is 0.25 dl/g, and, in the intrinsic viscosity of polymer, the number of fish eyes obtained polybutylene terephthalate system resin (PBT-2) of 3.4 piece / 100 cm<sup>2</sup> by 0.85 dl/g eventually. The film of 135-micrometer thickness was produced on Example 1 and the conditions, the biaxial stretching treatment of PBT-2 was increased 3x3 times with the drawing machine of the T.M. long company at 60 °, and the 15-micrometer-thick oriented film was obtained. The extension success percentage was shown in the 1st table.

[0019]The polybutyrene-terephthalate-resin pellet was manufactured like Example 1 except not having used comparative example 1 filter at all. The rate of an esterification reaction of oligomer in 1st-step esterification tub 2 exit in that case 87.3%, The intrinsic viscosity of the prepolymer in 98.2% and 1st step polycondensation tub 4 exit of the rate of an esterification reaction of oligomer in 2nd-step esterification tub 3 exit is 0.25 dl/g, and the intrinsic viscosity of polymer obtained polybutylene terephthalate system resin (PBT-3) of 1.21 dl/g eventually. The number of the fish eye in the film of this resin was 35.2 piece / 100 cm<sup>2</sup>, and was rough skin-like apparently. Film shaping and stretching treatment were performed like Example 1 using PBT-3, and the extension success percentage was shown in the 1st table. Examples 3 and 4 and comparative example 2PBT-1 (examples 3 and 4) and PBT-3 (comparative example 2) are used, With 3 sorts of Placo three-layer water-cooled tubular blown film molding equipment (3S01 type), -PBT layer thickness of 50 micrometers, and adhesion resin layer [acid modified polyethylene, The density of 0.90g / cm<sup>3</sup>, a melt index (MI=3.0g / ten parts) Mitsubishi Chemical "Modic F534A"]10 micrometers and in thickness, a polyolefin resin layer (it density-0.924-g-/cm<sup>3</sup> and) 3 sorts of tube shape three-layer water-cooled tubular blown film (overall thickness of 100 micrometers) with an MI0.7g/a low-density-polyethylene thickness [ 40 micrometers ] of 10 minutes was fabricated, and stretching

treatment was carried out to MD directions by one 4 times the draw magnification [ the extension temperature of 60 \*\*, and ] of this (example 3). Stretching treatment was carried out to one 3x3 times the draw magnification of this at the extension temperature of 60 \*\* (Example 4, the comparative example 2). Each extension success percentage was shown in the 1st table. [0020]

[Table 1]

第1表

	実施例 1	実施例 2	実施例 3	実施例 4	比較例 1	比較例 2
使用 P B T の種類	P B T-1	P B T-2	P B T-1	P B T-1	P B T-3	P B T-3
フィッシュアイ数(個/cm <sup>2</sup> )	6.3	3.4	6.3	6.3	35.2	35.2
層構成	単層	単層	3層	3層	単層	3層
延伸温度(℃)	50	60	60	60	50	60
延伸倍率	4倍	3×3倍	4倍	3×3倍	4倍	3×3倍
延伸フィルムの厚み(μm)	38	15	25	12	38	12
延伸成功率(%)	100	100	100	100	20	25

[0021](Note) Extension success percentage shows the extension success percentage at the time of extending 20 sheets.

[0022]

[Effect of the Invention]In this invention, polybutylene terephthalate system resin with few foreign matters obtained by continuous polymerization method is used as a raw material. Therefore, there are few fish eyes, it excels in molding stability, especially extension stability, and also the polybutylene terephthalate system resin oriented film excellent in appearance, internal visibility, design nature, etc. can be provided.